

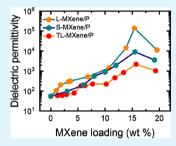
# Enhancement of Dielectric Permittivity of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene/Polymer Composites by Controlling Flake Size and Surface Termination

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Supporting Information

ABSTRACT: We report a strong effect of the MXene flake size and surface termination on the dielectric permittivity of MXene polymer composites. Specifically, poly(vinylidene fluoride-trifluoro-ethylene-chlorofluoroehylene) or P(VDF-TrFE-CFE) polymer embedded with large (ca. 4.5  $\mu$ m) Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> flakes achieves a dielectric permittivity as high as 10<sup>5</sup> near the percolation limit of 15.3 wt % MXene loading. In comparison, the dielectric permittivity of MXene/P(VDF-TrFE-CFE) using small (ca. 1.5 μm) Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> flakes (S-MXene) achieves a dielectric permittivity of 10<sup>4</sup> near the percolation limit of 16.8 wt %. Meanwhile, increasing the concentration of surface functional groups on the MXene surface (-O, -F, and -OH) by extending the etching time gives a dielectric constant of 2204 near the percolation limit of 15.7 wt %. The ratio of permittivity to the loss factor of our large flake composite is superior



to that of the small flake composite, and to all previously reported carbon-based fillers in P(VDF-TrFE-CFE). We show that the dielectric permittivity enhancement is strongly related to the charge accumulation at the surfaces between the two dimensional (2D) MXene flakes and the polymer matrix under an external applied electric field.

KEYWORDS: MXene flakes, size engineering, surface terminations, dielectric permittivity, microscopic dipole

#### 1. INTRODUCTIONS

Nanocomposites with conducting, semiconducting, and insulating fillers dispersed in poly(vinylidene fluoride)-based polymers have recently triggered renewed interest thanks to their potential in various electronic applications, including flexible electronics, energy harvesters, charge storage capacitors, and strain sensors. 1-6 In a previous report, 7 we investigated the dielectric constant enhancement of poly-(vinylidene fluoride-trifluoro-ethylene-chlorofluoroethylene) [P(VDF-TrFE-CFE)] using Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene flakes as the conducting filler. The MXene/P(VDF-TrFE-CFE) composite resulted in a dielectric permittivity over 100 000 near the percolation limit, which was the highest dielectric constant reported for P(VDF-TrFE-CFE)-based composites.8-12 Furthermore, the MXene/P(VDF-TrFE-CFE) composite may have a promising application in flexible electronics, fractional-order capacitors, and triboelectric generators.

MXenes, a new family of 2D transition metal carbides, nitrides, and carbonitrides with the general formula of  $M_{n+1}X_nT_{x}$  have recently raised considerable attention due to their promising characteristics in various applications, including energy storage, flexible electronics, water purifications, nanofiltration, photocatalysis, and biosensors. 13-20 In  $M_{n+1}X_nT_x$ , M is an early transition metal, X is carbon and/or nitrogen, T<sub>x</sub> represents the surface functional groups (e.g., OH, O, and/or F groups), and n = 1, 2, or 3. For two dimensional materials, including graphene oxide, 21 carbon nanotube, 22 and boron nitride,<sup>23</sup> the aspect ratio and surface chemistry are critical to the electrical and mechanical properties of their

nanocomposites. However, there have been no relevant reports on the size and surface chemistry effect of MXene nanosheets on the dielectric properties of MXene/polymer nanocompo-

In this study, we show that both the flake size and concentration of surface terminations are effective methods for improving the dielectric properties of MXene/polymer composites.

#### 2. EXPERIMENTAL SECTION

2.1. Preparation of MXene. The synthesis of few-layered Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> was prepared following a previous report.<sup>30</sup> Briefly, 1 g of  $Ti_3AlC_2$  powder (Carbon-Ukraine Ltd. particle size < 40  $\mu$ m) was slowly added to the etchant solution, which was prepared by adding 2 g of LiF to 40 mL of 9 M HCl. The mixture was stirred for 10 min and then was transferred to an oil bath. The temperature of the oil bath was kept at 35 °C and the mixture was stirred in the oil bath for 24 h. After etching, the suspension was washed with deionized water until the pH reached >6. Next, the sediment was again mixed with deionized water and sonicated in an ice bath for different times ranging from 30 min to 3 h to get few-layered Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> with different flake sizes. The sonication process was carried out under N2 bubbling. After sonication, the suspension was centrifuged for 10 min at 3500 rpm, the resultant supernatant with dark green color was collected and bubbled with N2 for future applications. The concentration of the Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> solution was measured by filtering specific amounts of the

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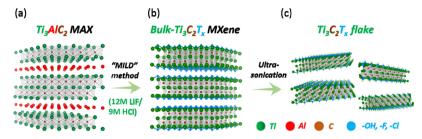


Figure 1. Schematic illustration of the structure of the (a) Ti<sub>3</sub>AlC<sub>2</sub> MAX phase, (b) bulk-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene after etching and delamination, and (c) MXene two dimensional (2D) flakes of different sizes obtained by ultrasonication.

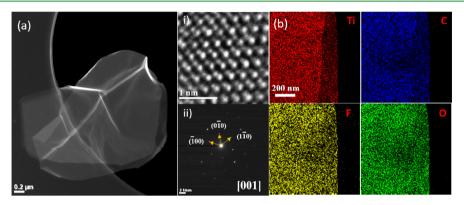


Figure 2. HRTEM image of (a) Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene flakes; Inset (i): Lattice-resolved HRTEM image of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> which shows the Ti atom hexagonal lattice. Inset (ii): SAED pattern of the Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene flake taken along the [001] axis. (b) STEM image of the Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene, and its corresponding elemental mapping.

colloidal solution through a polypropylene filter (3501 coated PP, Celgard LLC, Charlotte, NC), followed by overnight drying under a vacuum at 70 °C. A higher concentration of -F, -O, and -OH surface terminations were formed on the MXene surface after continuous etching for 96 h.

2.2. Fabrication of Nanocomposites. The previously collected Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene resultant supernatant was centrifuged for 10 min at 6000 rpm, and the precipitate of MXenes was collected and suspended in 3 mL of dimethylformamide (DMF) via shaking for 1 h. According to the intended MXene loadings, the desired quantity of P(VDF-TrFE-CFE) (61.5/30.2/8.3 mol % Piezotech S.A., France) was dissolved into the suspensions under continuous stirring for 30 min at 80 °C. After 2 h of gentle ultrasonication, the MXene/P(VDF-TrFE-CFE) suspension was directly cast onto platinum-coated silicon substrates. The composites were then dried overnight in a nitrogenprotected glovebox and were finally annealed at 70 °C in a vacuum oven for two days. Subsequently, top Ti (100 nm)/Au (50 nm) electrodes were deposited on the films (with an average thickness of 100  $\mu$ m) by electron-beam evaporation through a shadow mask for dielectric characterization.

2.3. Equipment and Characterization. The weight percent of MXenes in the polymer matrix was confirmed by thermogravimetric analysis (TGA). In addition, the structure and properties of MXene/ polymer composites were investigated by using XRD (Bruker D2 Phaser) and Fourier-transform infrared spectroscopy (FTIR) in the transmission mode (Nicolet iS10, Thermo Scientific). Raman spectroscopy was performed on a Horiba Aramis Raman microscope with 633 nm laser excitation. The MXene sheets were investigated with transmission electron microscopy (TEM) (Titan Cs Image), scanning electron microscopy (SEM) (Nova Nano), atomic force microscopy (AFM) (Asylum research), and X-ray photoelectron spectroscopy (XPS) (Amicus). Surface and cross-sectional images of composite films were observed with TEM (Titan Cs Image). Frequency-dependent capacitance was measured with an Agilent LCR meter (4980A) in the frequency range of 1k Hz to -100 kHz and an oscillation signal of  $\sim 50$  mV<sub>rms</sub> with a parallel equivalent circuit. The current density versus electric field (J-E) loops in our manuscript were derived from I-V curves measured using an Agilent B1500A system. The *J-E* loops were measured by using a direct current source with a field ramping rate of 50 V cm<sup>-1</sup> s<sup>-1</sup>. The dwell time was 0.5 s for each step.

## 3. RESULTS AND DISCUSSION

Figure 1 illustrates the synthesis process used to prepare MXene flakes (see the Experimental Section for the detailed process). Bulk-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXenes were first prepared from the Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> bulk MAX phase using the "MILD" method which involves using LiF and HCl for etching and delamination.<sup>24</sup> MXene 2D flakes with different sizes were obtained by changing ultrasonication time of the bulk Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>. After 1 h sonication, we obtained a flake size of 4-5  $\mu$ m, which are henceforth denoted as large MXene flakes (L-MXene). After 3 h sonication, we obtained a flake size of  $1-2 \mu m$ , which are henceforth denoted as small MXene flakes (S-MXene). The MXene flakes obtained by sequential 96 h etching and 1 h sonication are denoted as termination-rich large MXene flakes (TL-MXene). The L-MXene/P(VDF-TrFE-CFE), S-MXene/ P(VDF-TrFE-CFE), and TL-MXene/P(VDF-TrFE-CFE) composites were prepared by dispersing the L-MXene, S-MXene, and TL-MXene in the P(VDF-TrFE-CFE)/DMF solution, respectively, followed by casting on a platinum-coated silicon substrate, drying overnight in a glovebox, and finally annealing in an vacuum oven at 70 °C for 48 h. A film with an average thickness of 100  $\mu$ m was obtained, as measured by a profilometer, and the corresponding weight percent of the MXene in the composite was confirmed by TGA (Figure S1). Subsequently, Ti/Au contacts were deposited on the top of the MXene/polymer films through a shadow mask by e-beam

The high resolution TEM (HRTEM) image in Figure 2a shows the typical morphology of single-layered MXene flakes **ACS Applied Materials & Interfaces** 

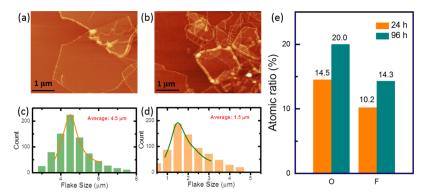


Figure 3. (a) AFM images of large-sized Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene (L-MXene) flakes deposited on mica. (b) AFM images of small-sized Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene (S-MXene) flakes. (c) Statistical distribution of the L-MXene flake size. (d) Statistical distribution of the S-MXene flake size. (e) The concentration of surface termination on MXene sheets after 24 and 96 h etching, measured using XPS.

that has been prepared through a sequence of etching and delamination processes discussed earlier. Inset (i) shows the lattice-resolved HRTEM image of the MXene sheets which indicates that Ti atoms form a hexagonal lattice. Inset (ii) depicts the selected area electron diffraction (SAED) patterns of the Ti<sub>3</sub>C<sub>2</sub>T<sub>r</sub> MXene sheets in Figure 2a obtained from the [001] direction, which confirms the hexagonal symmetry of the Ti sublattice. The marked reciprocal vectors represent their corresponding Miller indices of the planes in the real lattice. Furthermore, Figure 2b illustrates the scanning TEM (STEM) image of the Ti<sub>3</sub>C<sub>2</sub>T<sub>r</sub> MXene, and its corresponding elemental mapping, which shows a uniform distribution of Ti, C, F, and O elements in the MXene sheets.

Figure 3a shows the AFM image of L-MXene flakes with a 5.0 µm lateral size. Figure 3b shows the AFM image of overlapping S-MXene sheets with a 1.5  $\mu$ m lateral size. Figure 3c,d illustrate the size distribution of L-MXene and S-MXene, which reveal that the average lateral size of L-MXene and S-MXene is 4.5 and 1.5  $\mu$ m, respectively. The cross-sectional SEM image of MXene/P(VDF-TrFE-CFE), shown in Figure S2a, reveals that the MXene flakes dispersed inside the polymer matrix without aggregation, which was further confirmed by the AFM image of the same composite (Figure S2b). Both the Raman spectrum and FTIR of Ti<sub>3</sub>C<sub>2</sub>T<sub>r</sub> MXene flakes and MXene/polymer composites suggest that there are no vibrational changes during the mixing process (Figure S2c,d). The cross-sectional SEM images of S-MXene/P(VDF-TrFE-CFE) and TL-MXene/P(VDF)-TrFE-CFE) composites are shown in Figure S3.

Additionally, XPS was used to characterize the surface chemistry of MXene sheets after 24 and 96 h etching. The analysis reveals the presence of -OH, -O, and -F functional groups on the Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene surface (Figure S4). Compared with 24 h etching, the percentage of O (-O, -OH) and F increases from 14.5 and 10.2 to 20.0 and 14.3, respectively. These results indicate the oxidation of MXene flakes during the overetching process, from which we can conclude that the surface of MXene flakes after 96 h etching is rich in -F, -O, and -OH (Figure 3e).

Figure 4a displays the dielectric permittivity of L-MXene/ P(VDF-TrFE-CFE), S-MXene/P(VDF-TrFE-CFE), and TL-MXene/P(VDF-TrFE-CFE) composites as a function of filler loading, which indicates that the dielectric permittivity of these composites initially increases with MXene filler concentration. A dielectric constant > 100 000 was reached in the case of the composite with 15.3 wt % L-MXene in the terpolymer; in

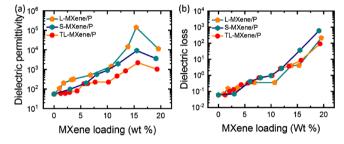


Figure 4. (a) Dielectric permittivity and (b) dielectric loss of the L-MXene/P(VDF-TrFE-CFE), S-MXene/P(VDF-TrFE-CFE), and TL-MXene/P(VDF-TrFE-CFE) composites versus MXene loading measured at room temperature and 1 kHz.

comparison, a dielectric constant of 10 000 was reached in the case of the S-MXene/polymer composite with a 16.8 wt % of S-MXene loading; the dielectric constant of the TL-MXene/ terpolymer composite reached 2204 near the percolation limit at around 16.0 wt %. The obvious degradation of dielectric permittivity of TL-MXene/P(VDF-TrFE-CFE) composites can probably be ascribed to the high dense concentration of negative surface functional groups on the TL-MXene surface, which could effectively decrease charge accumulation on the TL-MXene/polymer interface under the externally applied electric field. In all these cases, further increases in MXene loading leads to a drop in the dielectric constant value, which indicates that we have reached the percolation limit for all the L-MXene/P(VDF-TrFE-CFE), S-MXene/P(VDF-TrFE-CFE), and TL-MXene/P(VDF-TrFE-CFE) composites at 15-17 wt % MXene loading. The dielectric permittivity for composites that contain conductive fillers embedded in an insulating polymer matrix follows the power law according to the percolation theory. 25-29

$$\varepsilon_{\text{eff}} \propto \varepsilon_{\text{m}} (\varphi_{\text{c}} - \varphi_{\text{p}})^{-q} \quad \text{for} \quad \varphi_{\text{p}} < \varphi_{\text{c}}$$
 (1)

where  $\varepsilon_{\mathrm{m}}$  is the dielectric constant of the insulation matrix,  $\varphi_{\mathrm{p}}$ is the volume fraction of metallic fillers,  $\varphi_c$  is the volume fraction at the percolation threshold, and q is the critical

Figure 4b additionally presents the dielectric loss of L-MXene/P(VDF-TrFE-CFE) and S-MXene/P(VDF-TrFE-CFE) composites. Up to 10 wt % MXene loading, the dielectric constant and loss factor of the L-MXene/polymer composite increase 25 times (from 55 to 1425) and 5 times (from 0.06 to 0.35), respectively. Over the same range of

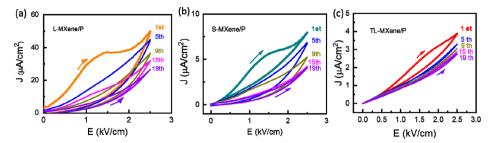


Figure 5. (a-c) Unipolar J-E loops measured with a positive field applied to the L-MXene/P(VDF-TrFE-CFE) and S-MXene/P(VDF-TrFE-CFE) and TL-MXene/P(VDF-TrFE-CFE) composites (with 8.0 wt % MXene), which have been prepoled with a negative field of 2.5 kV cm<sup>-1</sup>.

MXene loading (up to 10 wt %), the dielectric constant and loss factor of the S-MXene/polymer composite increases 10 times (from 55 to 560) and 9 times (from 0.06 to 0.61), and those of the TL-MXene/polymer composite increases 4 times (from 55 to 225) and 10 times (from 0.06 to 0.65). It is clear that the dielectric constant is more significantly enhanced, at a fixed MXene loading, when the composite uses L-MXene. Figure S5 and Table S1 in the Supporting Information specify the dielectric constant and dielectric loss of L-MXene/P(VDF-TrFE-CFE), S-MXene/P(VDF-TrFE-CFE), and TL-MXene/P(VDF-TrFE-CFE) composites at all the MXene loadings prepared in this study.

To obtain an insight into the cause of the different levels of dielectric constant enhancement by changing the MXene flake size, we performed unipolar measurements on both L-MXene/ P(VDF-TrFE-CFE) and S-MXene/P(VDF-TrFE-CFE) composites with 8.0 wt % MXene loading (see the Experimental Section for process details). Before these measurements, the composites had been poled using negative 2.5 kV cm<sup>-1</sup> for 5 min at room temperature. Figure 5a-c show the unipolar J-Ecurves of the L-MXene/polymer, S-MXene/polymer, and TL-MXene composites with the same 8.0 wt % of MXene loading, respectively. The unipolar J-E curves  $(0 \rightarrow 2.5 \text{ kV cm}^{-1})$ exhibit a bump at about 1.5 kV cm<sup>-1</sup> in the first cycle, which must be due to the current induced by some dipole reversal because the sample was previously poled by a negative voltage. After most "dipoles" had been aligned in the positive direction during the first positive electric field application, no bump was observed in either the increasing-field or decreasing-field curve in the following J-E loops (3rd to 19th). The leakagecorrected polarization can be calculated as follows

$$P(t) = \int_0^t [J(t) - J_{\mathrm{d}}(t)] \mathrm{d}t$$
 (2)

where J(t) is the measured total current density, including the current induced by dipole reversal and leakage, and  $J_{\rm d}(t)$  is the measured current density after several cycles of the electric field, which approximately represents the leakage current.

The leakage-corrected current and the derived remnant polarization of the L-MXene/P(VDF-TrFE-CFE) composite with 8.0 wt % MXene loading are 22.0  $\mu$ A/cm² and 14.0  $\mu$ C/cm², while those of the S-MXene/P(VDF-TrFE-CFE) composite with the same MXene loading are 4.1  $\mu$ A/cm² and 4.0  $\mu$ C/cm², and those of TL-MXene/P(VDF-TrFE-CFE) with the same MXene loading are 1.9  $\mu$ A/cm² and 0.8  $\mu$ C/cm², respectively. This result clearly indicates that the accumulated charges at the L-MXene/polymer interface (which form the switchable dipole) are larger than that of the S-MXene/polymer composite and TL-MXene/polymer composites, which means that the effective dielectric

permittivity of the L-MXene/polymer composite is higher than that of the S-MXene/polymer composite and TL-MXene/polymer with the same MXene loading.

## 4. CONCLUSIONS

We have developed a method to enhance the dielectric constant of MXene/P(VDF-TrFE-CFE) composites by engineering the flake size and concentration of surface functional groups. The MXene/P(VDF-TrFE-CFE) composite using large (4.5  $\mu$ m) MXene flakes reaches a dielectric permittivity as high as 10<sup>5</sup> near the percolation limit. In comparison, the MXene/P(VDF-TrFE-CFE) composite using small MXene flakes reaches a dielectric permittivity of 10<sup>4</sup> near the percolation limit, while the dielectric constant of the TL-MXene/P(VDF-TrFE-CFE) composite reaches to 2204 near the percolation limit of 16.0 wt %. These results were explained based on the accumulation of charges at the interfaces between the two dimensional (2D) MXene flakes and the polymer matrix, where the switchable microscopic dipoles are situated.

# ASSOCIATED CONTENT

# S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b09137.

TGA of L-MXene/P(VDF-TrFE-CFE), S-MXene/P-(VDF-TrFE-CFE) composites, and TL-MXene/P-(VDF-TrFE-CFE) composites, cross-sectional SEM image of the MXene/P(VDF-TrFE-CFE) composite, AFM image of the MXene/P(VDF-TrFE-CFE) composite, and Raman spectra and FTIR of MXene/P(VDF-TrFE-CFE) composites, cross-sectional SEM image of the S-MXene/P(VDF-TrFE-CFE) composite and TL-MXene/P(VDF-TrFE-CFE) composite, XPS spectra of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene etched for 24 and 96 h, dielectric constant of L-MXene/P(VDF-TrFE-CFE) composites, S-MXene/P(VDF-TrFE-CFE) composites, TL-MXene/ P(VDF-TrFE-CFE) composites, dielectric loss of L-MXene/P(VDF-TrFE-CFE) composites, S-MXene/P-(VDF-TrFE-CFE) composites, and TL-MXene/P-(VDF-TrFE-CFE) composites, and dielectric permittivity and dielectric loss of L-MXene/P(VDF-TrFE-CFE), S-MXene/P(VDF-TrFE-CFE), and TL-MXene/P(VDF-TrFE-CFE) composites with different MXene loadings (PDF)

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#### **Author Contributions**

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#### **Notes**

The authors declare no competing financial interest.

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